

INFLUENCE OF BACKGROUND ON THE FORM OF SPECTROCHEMICAL
CALIBRATION CURVES

H. Kaiser

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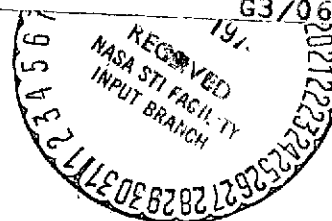
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16. Abstract Spectrochemical calibration curves are generally curved if the intensity of the spectrum background is not taken into account. If the background intensity is subtracted, a straight line is usually obtained. The equations for the (true) straight line and for the uncorrected calibration curve are set up. Each may be calculated from the other. In limited concentration ranges, the calibration curve may be approximated by a straight line. The equations for these "substitute" straight lines are derived. A simple formula is developed for the systematic errors of analysis generated by the use of a substitute straight line. A criterion for the necessity of a background correction is derived and depicted in the form of a graph. The theory is illustrated by an example. In the appendix, the effect on the background correction due to an incorrect filter value is described.			
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INFLUENCE OF BACKGROUND ON THE FORM OF SPECTROCHEMICAL CALIBRATION CURVES

H. Kaiser

I. Introduction

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The way in which the background in the spectrum must be taken into account in measuring the intensity ratio of two spectral lines is well known. Numerical tables for the required conversions were published in a work of M. Honerjäger-Sohm and H. Kaiser [2]. In this work an additional slide (U-slide) is recommended as a special accessory for the Owens analyzer [6]. This makes the background correction so simple that it can be carried out by trained technicians in the everyday work of a spectrochemical laboratory. Nevertheless, it would still be desirable to avoid the additional work always associated with the background correction, whenever the systematic errors in the analysis can be tolerated. This gives rise to the following questions:

When must the background be taken into account? What systematic errors will appear in the result of the analysis when the background is neglected?

If the background is ignored in drawing up a calibration curve, how can this curve be converted as a whole to the associated calibration curve with the background correction?

How can calibration curves in which the background is ignored be continued into the region of lower concentrations in which the background must be taken into account?

Since these questions have not yet been systematically treated, this will be the goal of the present work. To date,

*Numbers in the margin indicate pagination in the foreign text.

only examples have been published, e.g. in a report of G. Balz [1], which shows how a calibration curve bent by the influence of the background is broadened by the correction.

II. Calibration Lines and Curves

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As in previous works, we use Y for the logarithm of an intensity and ΔY for the logarithm of an intensity ratio. We wish to assume that the universal main calibration curve of the spectrochemical method under consideration is precisely a straight line, once the background has been taken into account. This assumption will be valid in most cases. We therefore formulate the following calibration equation:

$$\log k = \eta \Delta Y_G + \log k_0. \quad (1)$$

We use the Greek letter η for the slope of the calibration line, by analogy with the symbol γ for the slope of the density curve. k_0 is the concentration at the fixed point ($\Delta Y_G = 0$). The index G to ΔY is to indicate that the intensity ratio is to be taken between the analyzed line L of the alloying element Z and a line of the base element G . When we take

$$\Delta Y_G = Y_L - Y_G$$

we must first calculate Y_L by a background correction from Y_{L+U} [U = background]; this is because the immediate result of the density measurement is just the intensity for the line and background ($L + U$) together.

We now introduce the intensity ratio of the analysis line of the alloying element Z against its background U_Z : $\Delta Y_U = Y_L - Y_{U_Z}$, and using the identity

$$\Delta Y_G = \Delta Y_U + (Y_U - Y_{U_Z})$$

we obtain from (1) the general equation for the calibration curve measured against the background:

$$\log k = \eta \Delta Y_U - \eta(Y_G - Y_{U_Z}) + \log k_0. \quad (2)$$

In general, $(Y_G - Y_{U_Z})$ is still a function of k . So that the calibration curve against the background will also be a straight line, we wish to assume that $Y_G - Y_{U_Z} \sim \log k$. Accordingly, we can assume, without loss of generality, that $Y_G - Y_{U_Z}$ is constant; otherwise there would just be a different value for η in (4).

We introduce a new constant by the equation

$$\log k_U = \log k_0 - \eta(\overline{Y_G - Y_{U_Z}}) \quad (3)$$

k_U is the concentration at which the intensities of the line and the underlying background are equal. The bar above the expression in parentheses indicates that the mean value of this quantity /299 should be taken from different calibration spectra. For the equation of the calibration line measured against the background, we obtain

$$\log k = \eta \Delta Y_U + \log k_U. \quad (4)$$

We will call this form the (true) calibration line to distinguish it from other calibration curves to be considered later. Assuming that the true calibration curve is a straight line at this point will not involve any loss of generality in subsequent considerations. This assumption is valid in most cases; furthermore, later developments will show that deviations from the straight line can be directly worked into the theory (see Eqs. (5) and (6)). However, the further assumption that $Y_G - Y_{U_Z}$ is constant (or at least a simple, monotonic function of k) is necessary. We can make statements about the influence of the background on the calibration curve as a whole only when we know the behavior of the background as a whole, i.e. as a function. If the background depended on incidental factors, e.g. certain additives in the specimens, nothing at all could be said about the calibration curve without the background correction; there

would be no alternative but to deduct the background from the analysis lines in each individual case and to use the main calibration curve (1). Equation (4) with ΔY_U could not be formulated. Nevertheless, the requirements on the constancy of $Y_G - Y_{U^Z}$ do not have to be as strict as e.g. those on the constancy of the measured value ΔY_G in repeated spectra of the same specimen in a method for precise quantitative analyses. Namely, using the abbreviation

$$Y_{L+U} - Y_U = \log x,$$

the quantity D relevant for the background correction is equal to $\log x - \log(x - 1)$ [2]. In transferring the background fluctuations to the correction factor D, it is the derivative which is crucial

$$\frac{dD}{d \log x} = \frac{1}{x-1}.$$

This transfer factor is smaller than 1, as long as the line by itself is stronger than the underlying background; in that case, $x > 2$.

If the line is not too weak in comparison with the background -- and that will usually be the case in precise quantitative analyses -- inhomogeneities in the intensity of the background /300 will have a diminished effect on the correction. In that case, taking the correction for a mean background intensity will not cause any large errors. Only experience will show what is permissible in such cases.

If the background for different specimens is not quite equal, no reasonable calibration curve would be obtained by taking the value of $\Delta Y_U = Y_L - Y_U$ from the measurements for each specimen. However, we need Eq. (4) for the true calibration line expressed in terms of the background. Therefore, we express

the line intensities in terms of a mean normal background, calculating ΔY_U from ΔY_G by adding $\frac{Y_G - Y_{U_Z}}{Z}$. This puts everything in the definition of k_U in Eq. (3).

We should also point out that so far we have spoken only of the background lying behind the analysis line. We do not care about the background at the point of the base line. If its ratio to the base line is constant, it does not have to be taken into account, since it would only change the value of ΔY by an additive constant; if the ratio is variable, the background must always be deducted.

We now formulate the equation for the bent calibration curve, obtained when no background corrections are made. All associated quantities are designated by an apostrophe. For example,

$$\Delta Y'_U = Y_{L+U} - Y_{U_Z}.$$

We obtain the equation of this (true) calibration curve by combining the equation for a straight line with a correction function h .

$$\log k = \eta' \cdot \Delta Y'_U + \log k'_U + h(\Delta Y'_U). \quad (5)$$

For the time being, the constants η' , k'_U , and the function h will remain completely undetermined; the power of this purely formal approach will become evident later. We subtract (4) from (5) and, using the abbreviation $v = \log k'_U - \log k_U$, we obtain

$$h(\Delta Y'_U) = \eta \cdot \Delta Y_U - \eta' \cdot \Delta Y'_U + v. \quad (6)$$

We set the quantity obtained directly from the measurements, namely $\Delta Y'_U$, equal to $\log x$.¹ Then

¹At this point we introduce the neutral letter x for the intensity ratio, because we wish to treat it as a purely computational variable. It would just be a nuisance if we dragged along the idea of its physical significance.

$$\Delta Y_U = \log(x-1).$$

This is because, returning to the intensities themselves,

$$\Delta Y_U = \log(I_L/I_U),$$

and

$$\Delta Y_U' = \log \frac{I_L + I_U}{I_U} = \log \left(\frac{I_L}{I_U} + 1 \right).$$

From (6), we then obtain:

$$h(x) = \eta \log(x-1) - \eta' \log x + v. \quad (7)$$

If values are now assigned to the constants η' and v , the related function $h(x)$ can be calculated for each value of x . From (5), we then acquire the equation of the true calibration curve, in the derivation of which no background correction was made. This equation can be used e.g. to find the deviations of the calibration curve (5) from the calibration line (4). To do this, we must merely set $\eta' = \eta$ and $v = 0$.

III. The Equivalent Calibration Line

It is tempting to assume that the differences between (4) and (5) calculated in this way would give the systematic errors in the analytical values when the background correction (i.e. using a bent calibration curve) is omitted and a straight line used instead, because the curvature is hardly noticeable. This assumption is wrong. In fact, the straight line employed for analysis in such cases is not the true calibration line, but a substitute calibration line, replacing the true calibration curve in the relevant measuring range.

Figure 1 shows the true state of affairs. The true calibration line (designated ΔY_U) and the true calibration curve $\Delta Y_U'$

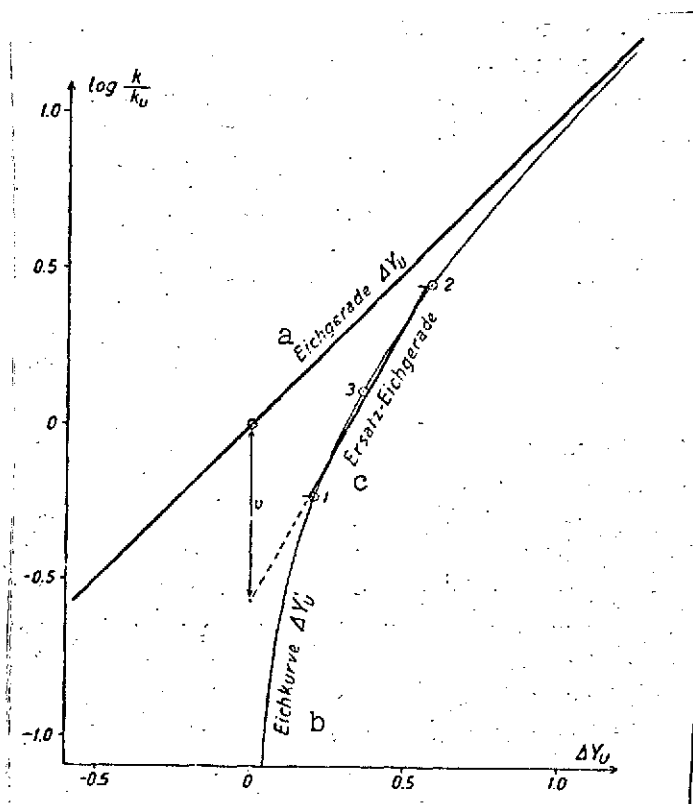


Fig. 1. Calibration line (ΔY_U), calibration curve (ΔY_U), and substitute calibration line for a limited concentration range. (All with respect to the mean normal background.)

Key: a. Calibration line
b. Calibration curve
c. Substitute calibration line

differ only slightly at high concentrations when the line of the element to be determined is strong in comparison with the background. However, the weaker this line becomes, the further downward the calibration curve is pulled by the influence of the background. Finally, it approaches asymptotically the vertical line $\Delta Y_U = 0$, which corresponds to the intensity of the background by itself.

How is the substitute calibration line produced? Assume that we have three specimens with reliably determined concentrations k_1 , k_2 , and k_3 for the main calibration of the procedure. k_1 is at the lower end of the intended measuring range, k_2

at the upper end, and k_3 roughly in the middle (on the logarithmic /302 scale). From the calibration spectra we find three measurements $\Delta Y_{U1} = \log x_1$, $\Delta Y_{U2} = \log x_2$, and $\Delta Y_{U3} = \log x_3$. If we ignore measuring errors, the associated points must lie precisely on the calibration curve, as shown in Fig. 1. Since we have ignored the relatively weak background, and not even measured it, we know nothing about the true calibration curve and its curvature; we see only three calibration points, which do not lie precisely on a straight line. If the deviation from a straight line is not too

blatant, we will be inclined to draw a straight line past the three points in such a fashion that the differences are minimized. We are misled by our desire to make linear interpolations, and we might even assume that the observed curvature is not real, but /303 just simulated by erroneous analytical values for the calibration specimens.

Instead of the true curved calibration curve, we draw the substitute calibration line! One such line is drawn in Fig. 1.

It is important that a substitute calibration line is always associated just with a fixed measuring range, in which it represents the best approximation to the calibration curve. Each measuring range has its own substitute calibration line. We now wish to know how the substitute calibration line is determined.

If we knew the position and shape of the true calibration curve, the substitute calibration line could be determined e.g. from the requirement that the mean square error over the entire intended measuring range should be minimized. For the time being, however, we do not know the true calibration curve, but have only three calibration points. (This is actually fortunate, since the least squares fit would result in equations which cannot be solved!) In such a case we proceed as follows: first we connect the two outer measurements by a straight line and then, maintaining the same slope, we shift the line toward the middle measurement until all three points are equally distant from this line.

If in (7) we consider n' and y the constants of the substitute calibration line, then h is just the difference between a measured point on the true calibration curve and the substitute calibration line. The above rule for drawing the substitute calibration line on the basis of the three measured points thus yields the following conditions:

$$h(x_1) = h(x_2); \quad (8a)$$

$$h(x_1) = -h(x_3). \quad (8b)$$

Together with (7), (8a) gives the equation for the slope η' of the substitute calibration line

$$\eta' = \eta \frac{\log(x_1 - 1) - \log(x_2 - 1)}{\log x_1 - \log x_2}. \quad (9)$$

(8b) and (7) imply

$$v = \frac{\eta'}{2} (\log x_1 + \log x_3) - \frac{\eta}{2} (\log(x_1 - 1) + \log(x_3 - 1)). \quad (10)$$

v was the abbreviation for $\log k_U - \log k'_U$. We thus have the intersection of the substitute calibration line with the vertical line $\Delta Y = 0$, i.e. the fixed point relative to the background. The concentration k'_U associated with this fixed point will never appear as an analytical result as long as we make no background correction and use only the substitute calibration line; since the line and background together are always greater than the background by itself, $\Delta Y'_U = Y_{L+U} - Y_U$ can never be zero. The number v gives the displacement of the fixed point of the substitute calibration line from that of the true calibration line (see Fig. 1).

If we wish to return from background-based calibration lines to those based on a line of the base element, we merely apply Eq. (3) to the calibration line and the substitute calibration line, thus obtaining for the displacement of the two fixed points based in the usual way on the lines of the base element

$$\log k_0 - \log k'_0 = v + (\eta - \eta') (Y_G - Y_{U_Z}). \quad (11)$$

In general, the fixed point k'_0 of the substitute calibration line based on the line of the base element can naturally occur as a

result of the analysis, namely when the intensity of the base line is greater than that of the background at the point of the alloying-element line. Figure 2 shows how these different calibration lines are related.

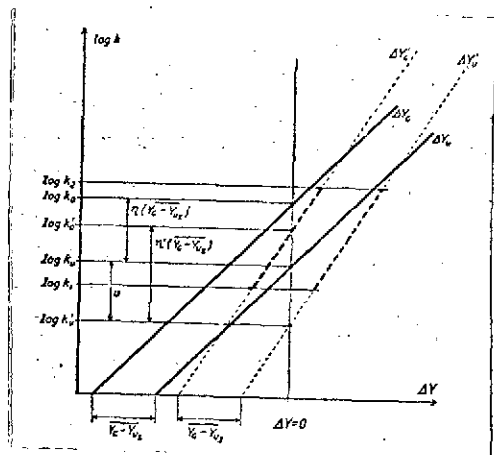


Fig. 2. Relative positions of calibration line and associated substitute calibration line (broken line), with respect to the background or the line of the base element.

tion and ignore the resulting curvature of the calibration curve. We thus have all the facts necessary for answering the questions posed in the introduction.

We first wish to inquire into the position of the middle calibration point, which is used in determining the substitute calibration line. If we could freely choose the concentration of the alloying element in this calibration specimen, it would certainly be best to take the middle measurement at the point where the calibration curve is furthest from the substitute calibration line. In order to find this point x_a , we must differentiate (7) with respect to x and set the derivative equal to zero. We find

$$x_a = \frac{\eta'/\eta}{\eta'/\eta - 1} \quad (12)$$

This point of maximum difference is not in general in the middle of the range, because the curvature of the true calibration curve is not uniform.

IV. Manipulating the Conversion Formulas

We now wish to show how the different conversion problems can be solved with the aid of the formulas which have been developed. We will always start from the normal case, i.e. the calibration lines and curves being expressed in terms of a line of the base element G. The calibration equations expressed in terms of the background appear only during the conversion.

1) Given: The true calibration line (with background correction).

To find: The true calibration curve (without background correction).

We know the constants n and k_0 of the calibration line (1). To make the conversion, the quantity $Y_G - Y_{U_Z}$ must be measured in the spectra of the specimens. We must check whether $Y_G - Y_{U_Z}$ in the spectra of the different specimens has the same value within the unavoidable measuring error. Only then will the conversion make sense. From all the spectra, we take the mean value $\overline{Y_G - Y_{U_Z}}$.

Now we calculate $\log k_U$ from (3), and then have the equation of the calibration line expressed in terms of the background (4). From this equation, we calculate the value of $\Delta Y_U = \log(x - 1)$ for however many different values of k as we wish. With these numbers, we consult the numerical tables on the Seidel transformation (see [2]) and take the corresponding values of $\log x = \Delta Y'_U$ from the first column of the table. Finally, we subtract $Y_G - Y_{U_Z}$ from these numbers, thus obtaining $\Delta Y'_G$. With these pairs of values $(\log k, \Delta Y'_G)$, we draw the desired true calibration

curve (without background correction), expressed in terms of a line of the base element.

This conversion is important for the following reason: we can use the calibration curve to prepare for the Owens analyzer a concentration scale already containing the background correction. If we wished to determine the calibration curve directly from measurements on a few calibration specimens, it would not be possible to do it precisely, because interpolations between the measured points on the curved graph will not be very good, and because errors in the concentration figures for the calibration specimens as well as measuring errors will not be recognizable. /306 Therefore, it is much better to first determine the true calibration line (with background correction) and from it to calculate the calibration curve (without background correction). The calibration line can be obtained with sufficient precision from the measurements on two or three calibration specimens; inaccuracies in the concentration figures show up, and can be checked and nullified, the same being true of measuring errors. By this detour, we obtain more reliable figures for the analysis.

2) Given: The true calibration line (with background correction).

To find: The substitute calibration line (without background correction) for the range of concentrations from k_1 to k_2 .

We again have η , k_0 , and $\overline{Y_G - Y_{U_2}}$, and from them calculate, with the aid of (3), the equation of the true calibration line, expressed in terms of the background (4). We substitute k_1 and k_2 into this equation, obtaining the associated values of $\Delta Y_{U_1} = \log(x_1 - 1)$ and $\Delta Y_{U_2} = \log(x_2 - 1)$. For this purpose, we find -- most conveniently by using the numerical table for the Seidel transformation -- the values of $\log x_1$ and $\log x_2$. Equation (9) now gives the slope η' of the substitute calibration

line. We substitute this value of η' in (12), thus obtaining x_a for the point of maximum difference. In (10), we replace x_3 by x_a , thus acquiring v . Finally, Eq. (11) supplies the displacement of the fixed points. All that remains is to draw a straight line of slope η' through the fixed point with the coordinates $\log k'_0$ and $\Delta Y = 0$, the line interval extending along the vertical axis from $\log k_1$ to $\log k_2$. We then have the desired substitute calibration line $\log k = \eta' \Delta Y'_G + \log k'_0$. From (7), we can now calculate the improvement for each measurement which must be added to the analytical result. These improvements can be recorded once and for all in a table or a curve.

3) Given: A substitute calibration line for the range between k_1 and k_2 , determined by three calibration points at k_1 , k_3 , k_2 .

To find: The true calibration line for an arbitrary measuring range (with background correction).

Given are η' , k'_0 , k_1 , k_2 , k_3 , and $\overline{Y_G - Y_U}$. First we apply Eq. (3) to the numbers represented by symbols with apostrophes, thus obtaining $\log k'_U$. Then we know the equation of the substitute calibration line with respect to the background. For k_1 , k_2 , and k_3 , we calculate the values of $\Delta Y'_U = \log x$, if the latter are not already given by the calibration measurements, which is /307 preferable. For this purpose, we find $\log(x - 1)$ from the table of the Seidel transformation. These numbers and Eq. (9) furnish the slope η of the true calibration line, and then Eq. (10) gives the distance v between the fixed points. From (11), we obtain $\log k_0$ for the fixed point of the true calibration line, which we can draw with slope η through the fixed point with the coordinates $\log k_0$ and $\Delta Y = 0$.

If the substitute calibration line is to be determined by more calibration points than just three, the rule given in III. for its construction must be modified accordingly. For the

conversion, we need only three points; the middle point is chosen so that the conditions (8) are satisfied.

4) Given: A substitute calibration line for the range between k_1 and k_2 , determined by three calibration points at k_1 , k_3 , k_2 .

To find: The substitute calibration line with the best fit for another range from k_I to k_{II} .

This problem is solved in two steps. First, as in 3), we determine the true calibration line, and then, as in 2), we determine the new substitute calibration line for the range from k_I to k_{II} .

The two problems (3) and 4) have great practical significance. Suppose that by taking several careful calibration spectra, we had obtained a very accurate main calibration curve for determining an alloying element Z in a base element G. This calibration held in a region of higher concentrations of Z, in which the background behind the powerful analysis line of Z could be ignored. The calibration curve is drawn as a straight line; it is therefore a substitute calibration line, valid only in the range encompassed by the calibration specimens. Now suppose we take the spectrum of a specimen in which the line of Z is much fainter, so that the background must be taken into account. If we just extrapolated the substitute calibration line valid for high concentrations, the resulting Z concentration would be much too high. What can be done? One would be very reluctant to remeasure the old calibrating photographs -- if they are still around -- and to make the background correction on all the individual values, although it would be very nice to exploit the high precision of the old calibration for the new problem. However, if experience has shown that the background at the Z line is constant, the new calibration can be computed with the aid of the above formulas.

All we have to do is find $Y_G - Y_{U_Z}$. This can often be done from the spectrum of the unknown specimen; there may be other spectra for specimens of the same type, so that a mean value can be taken. /308 Once we have this number, we can either calculate the true calibration line (with background correction) or a substitute calibration line for the lower range.

In view of such cases, which come up quite often in the ongoing work of a technical laboratory, it is a good idea to simultaneously determine the number $Y_G - Y_{U_Z}$ in each calibration. This makes it possible to later expand the range of validity of the calibration. As was shown in a previous work [4], this number must also be known in order to calculate the detection limit attainable with a given procedure and the minimum concentration at which a prescribed accuracy can be adhered to (determination limit).

This answers all the questions of the Introduction except for the first very general one. Before we deal with this one as well, we wish to make the previous discussion more vivid by means of a numerical example.

V. Numerical Example

The numerical values of the example come from measurements on three aluminum specimens of the alloy type AlMg5, manufactured as calibrating electrodes by the Wielandwerken in Ulm. These specimens had been precisely analyzed. The spectra were taken in accordance with the procedure AV 22 (Zeiss Druckschrift Mess 266/III). For this work, only the data on the spark discharge and the slit width of the spectrograph are important, because they determine the intensity of the background. The sparks were produced with the Feussner spark generator; the capacitance in the spark circuit was 8100 pF, and the only self-inductance was that of the leads, about $6 \cdot 10^{-6}$ H. The slit width of the Zeiss spectrograph Q 12 was 0.035 mm. Of interest were the calibration curves for manganese. The

measured line was Mn 2949 Å and the base line was Al 3050 Å. The Y values were calculated in the usual way from the optical densities, then ΔY , both with and without subtraction of the background at 2949 Å. These values are in columns 5 and 6 of Table 1. These are mean values from three spectra apiece. In the fourth column are the values of $\log k$. They are taken for the concentrations expressed in terms of the Al content of the specimens. These concentrations must be calculated from columns 2 and 3.

TABLE 1.

1 Specimen	2 % Mn	3 % Al	4 $\log k$	5 $\Delta Y'_G$	6 ΔY_G	7 $Y_{L+U} - Y_U$
5 U	0.10	93.0	- 0.968	- 0.352	- 0.715	0.247
5 T	0.28	94.0	- 0.526	- 0.104	- 0.248	0.550
5 S	0.45	93.5	- 0.318	+ 0.066	- 0.041	0.661

With the numbers in Table 1, the true calibration line for the Mn determination (column 6) and the substitute calibration line for the range from 0.10 to 0.45% Mn (column 5) can be drawn. The measurements are plotted in Fig. 3. For the constants of the true calibration line we find:

$$n = 0.965 \text{ and } \log k_0 = -0.283.$$

(This line is not drawn in Fig. 3, but instead the true calibration line calculated from the substitute calibration line.)

The constants of the substitute calibration line are:

$$n' = 1.555 \text{ and } \log k'_0 = -0.393.$$

This line is drawn as an interval in Fig. 3, and the fixed point k'_0 is indicated. The deviations of the three measurements

from the straight line are so small that one would hardly draw a nonlinear calibration curve through them if one knew nothing of the interrelationships. The systematic errors in analysis which would result from this carelessness will be discovered as we calculate through the example.

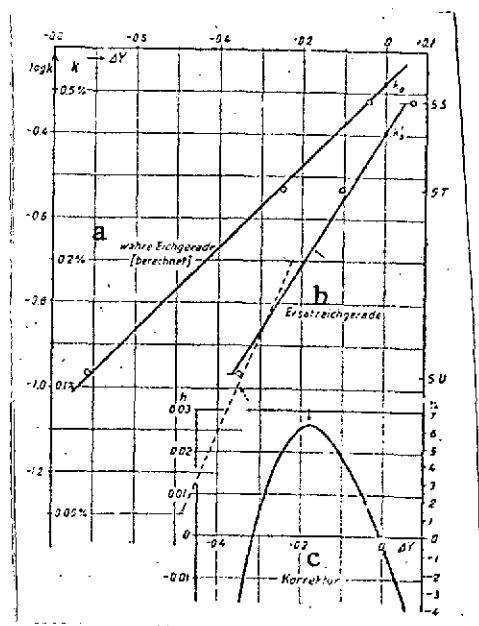


Fig. 3. True calibration line and substitute calibration line for determining manganese in aluminum alloys. (Bottom right: correction curve for substitute calibration line; broken line: substitute calibration line for 0.05% through 0.2%))

Key: a. True calibration line (calculated)
b. Substitute calibration line
c. Correction

up the corresponding value of $\Delta Y_U = \log(x - 1)$ and find -0.091, 0.344, and 0.573.

For the calculation, we require $\overline{Y_G - Y_{U_Z}}$. The mean value for this quantity, determined from numerous spectra, was 0.610. The background for the middle specimen was somewhat fainter than for the two outer ones; $Y_G - Y_{U_Z}$ was thus not quite constant, but about 0.05 larger for the middle specimen. However, this variability has no major influence on the calculation, so we express everything in terms of a normal value for the background.

We now calculate the values of ΔY_U^i by adding 0.610 to each of the numbers in column 5. This gives 0.258, 0.506, and 0.676, respectively. For each of these numbers $\Delta Y_U^i = \log x$, we look

With these numbers, we obtain from (9) and (10) $\eta = 0.980$ and $v = 0.470$.

Equation (11) then supplies $\log k_0 = -0.274$. Thus we have found the constants of the true calibration line; they are only slightly different from those previously derived directly from the measurements. The calculated calibration line is drawn in Fig. 3; it fits well with the measurements. If for $\overline{Y_G - Y_{U_z}}$, instead of 0.610, we had employed the corresponding value of 0.599 for specimen 5U, we would have found $\eta = 0.962$ and $\log k_0 = -0.271$. The slope would then agree better, but the line would be situated somewhat above all three measured points. Calculating with a mean value for the background was therefore correct.

By Eq. (12), the point of maximum error on the substitute /310 calibration line is $x_a = 2.70$. The associated ΔY_G^1 is $\log x_a - 0.610 = -0.179$. This point is indicated in Fig. 3 by an arrow. The improvement $h(x_a)$ is ± 0.026 , corresponding to 6.2% of the concentration. Such large systematic errors could therefore occur if this substitute calibration curve were used without correction. By comparison, the random measuring errors in the analysis are much smaller, because the dispersion of the method is less than 2%. The high internal accuracy of such a complete analytical method can therefore be exploited only when the influence of the background is taken into account in the analysis.

The corrections which must be made in using substitute calibration lines can be calculated from (7). The correction function is plotted in Fig. 3 below the substitute calibration line. This graph shows the great increase in correction required outside the range of validity of the substitute calibration line.

When the background in the spectra of all specimens to be analyzed by the same calibration system is roughly constant, so that the theory is applicable, it is then beneficial to establish the

corrections once and for all, e.g. in the form of the correction curve for the substitute calibration line. Then, the background does not have to be measured in each analysis, thus avoiding the random errors which would be introduced into the analysis by an additional measurement of the background density.

We now wish to discover the substitute calibration line for a low concentration range. We pick the range between 0.2% and 0.05%, which overlaps the lower end of the old range.

$$k_I = 0.05; \log k_I = -1.3; k_{II} = 0.2; \log k_{II} = -0.7.$$

With the previously calculated values for the true calibration line, we obtain from (3) $\log k_U = -0.872$, and thus for the equation of the calibration line with respect to the background

$$\log k = 0.98 \cdot \Delta Y_U - 0.872.$$

In it we substitute the values for $\log k_I$ and $\log k_{II}$, thus obtaining for the associated $\Delta Y_U = \log(x - 1)$: -0.437 and $+0.176$. The corresponding values of $\log x$ are 0.137 and 0.398 . Now we can calculate η' from (9). $\eta' = 2.28$; then from (12), $x_a = 1.75$ with $\log x_a = 0.243$ and $\log(x_a - 1) = -0.125$. We substitute this value of x_a in Eq. (10), and obtain the value 0.707 for v . From (11), we then get $\log k'_0 = -0.189$. Thus we have the constants for the new substitute calibration line and can draw it. It is the broken line in Fig. 3. From (7), we now calculate the maximum value for the correction in the new range by substituting the numbers for x_a . We find $h(x_a) = 0.030$, corresponding to 7.2% of the content.

Lastly, we also wish to calculate what would have happened if we had used the old substitute calibration line down to 0.05%. For this purpose, using η' and v of the old substitute calibration line as well as the logarithms associated with 0.05%, which we have already calculated, we obtain from Eq. (7):

$$h(0.05\%) = -0.98 \cdot 0.437 - 1.555 \cdot 0.135 + 0.470 = -0.168\%$$

This corresponds to 47.2% of the content. Thus, instead of the true Mn content of 0.05%, we would have obtained much too high a value, namely 0.074%, if we had extended the old substitute calibration line downward.

VI. When Is the Background Correction Necessary?

/311

It would be very bothersome if we had to calculate through all the formulas every time in order to decide whether the influence of the background is so strong that it must be taken into account, or whether we can use a substitute calibration line for the analysis. We need a simple criterion.

Obviously, the smaller a concentration range, the better a substitute calibration line drawn for it will be. If we wish to answer the question, we must therefore prescribe the extent of the concentration range. Another relevant factor is the intensity of the analysis line in comparison with the background. This factor can be gauged by means of the quantity ΔY_U .

$$\Delta Y_{L+U} - Y_U = \Delta Y'_U = \log x.$$

The analysis line is relatively faintest in the spectrum of a specimen whose content lies at the lower end of the prescribed range. Thus we are interested in the smallest value of $\Delta Y'_U$, the value at the lower end of the range. This we will designate with the symbol ΔU ;

$$\Delta U = \Delta Y'_U = Y_{L+U} - Y_U \text{ at the lower limit of the concentration range of a calibration.}$$

From the formulas in this paper, we can now calculate the maximum error which can occur within a given concentration range when ΔU has a specific value. The maximum error in a given concentration range occurs at the concentration corresponding to

x_a . If we first substitute x_a in (10) and then in (7), we find:

$$2h(x_a) = \eta \log \frac{x_a - 1}{x_1 - 1} + \eta' \log x_1 - \eta' \log x_a. \quad (13)$$

In order to calculate this quantity as a function of the concentration range k_2/k_1 and of ΔU , we proceed as follows: we take a normal value for η , and set $\eta = 1$. Then, because of (4),

$$\log(k_2/k_1) = \log(x_2 - 1) - \log(x_1 - 1).$$

From this we obtain:

$$x_2 = 1 + \frac{k_2}{k_1}(x_1 - 1). \quad (14)$$

The given value of ΔU is $\log x_1$; thus we also have $\log(x_1 - 1)$. Thus we have all the quantities we need to calculate the maximum /312 error from (13) via (9), (12) and (10).

This is done in Fig. 4. On the left side is given the error in the logarithm of the concentration, and on the right the corresponding error as a percentage of the concentration. There are curves for concentration ranges of various widths, from 1:2 to 1:1000.

An example will illustrate the use of Fig. 4:

We stipulate that the systematic error in analysis should be less than 2%. The calibration covers a concentration range of 1:10, e.g. the range from 0.04% to 0.40% or from 1.2% to 12%. In that case, according to Fig. 4, the crucial value of ΔU must be larger than 0.8 if the background correction is to be eliminated. In order to clarify the meaning of this condition, recall that in the middle UV, the slope of the density curves is roughly 1, so that $\Delta Y \approx \Delta S$ for densities in the upper straight portion of the density curve (S greater than about 0.5). The condition $\Delta U > 0.8$ would then mean that the density difference between line + background

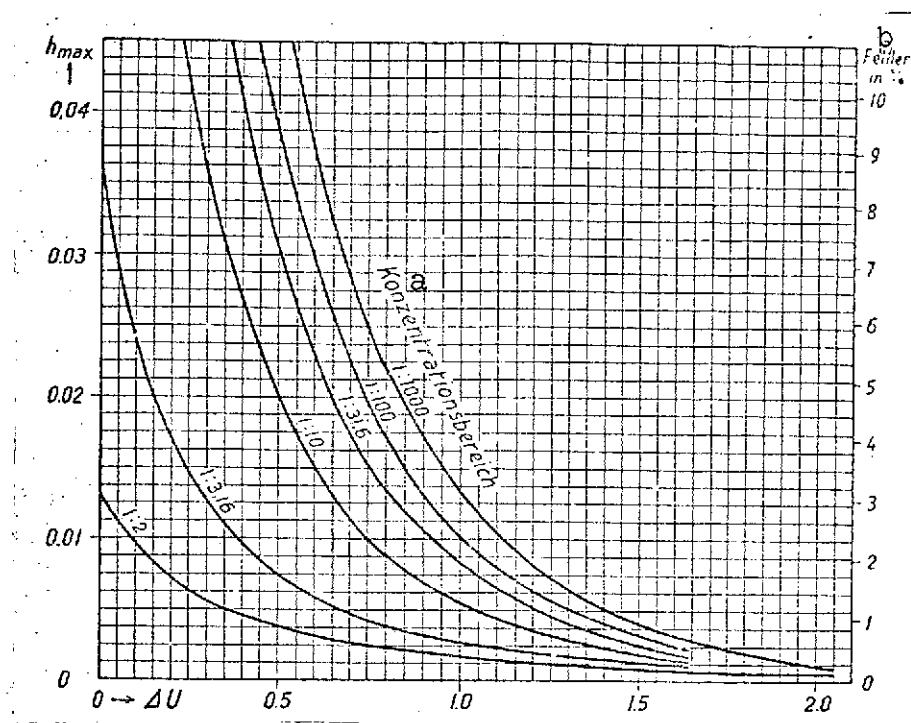


Fig. 4. Maximum systematic error in neglecting background. (Slope of calibration curve $\eta = 1$; $\Delta U = \log x_1 = Y_{L+U} - Y_U$ for lower end of range).

Key: a. Concentration range
b. Error

and the background by itself at the lowest concentration in the calibrating range must be at least 0.8. The condition is therefore relatively strict.

The curves in Fig. 4 hold for $\eta = 1$. However, they can be used for any other values of η by multiplying the numbers on the error scale by η . According to (9), $\eta' \sim \eta$, therefore according to (10), $v \sim \eta$ as well, and thus by (12) and (7), $h(x_a) \sim \eta$ too. /313

Figure 4 is a kind of alert table for work in a spectrochemical laboratory; it gives a complete answer to the first, important question of the introduction.

In Fig. 4, it is striking that the curves for $\Delta U \rightarrow 0$ tend toward finite limits. In other words, neglecting the background

does not produce arbitrarily large errors, even when the line is barely visible against the background. Z. Bochnicek has derived the following formula for these limits:

$$2h(x_a)_{\Delta U \rightarrow 0} = \log \frac{\frac{k_2}{k_1} - 1}{\log \frac{k_2}{k_1}} + \frac{\log \frac{k_2}{k_1}}{\frac{k_2}{k_1} - 1} + \log \frac{\log e}{e}. \quad (15)$$

This formula is obtained by expanding $\Delta U = \log x_1$ for small values, $\log x_1 \approx (x_1 - 1) \cdot \log e$, and then running through Eqs. (9), (12), and (13).

I am indebted to Z. Bochnicek, who calculated the numerical values for the curves in Fig. 4, and to A. Richter for her careful preparation of the spectra and analyses for the numerical example in V.

Appendix. Background Correction with Incorrect Filter Value

In the work on systematic errors in analysis [5], the following question was left open: what is the effect on the background correction if all the intensity ratios have been calculated with an incorrect filter value ΔY_m ? We now have the means to answer this question.

As in [5], we again designate the true values with small letters, and those calculated with the incorrect filter value with capital letters. The error factor of the filter value is $f = \Delta Y_m / \Delta Y'_m$. All calculated $\Delta Y'$ are incorrect by this factor;

$$\Delta Y' = f \Delta y'. \quad (16)$$

The correction factor D is tabulated in [2] as a function of

$$\Delta Y'_U = Y_{L+U} - Y_U$$

for clarity, we write $D(\Delta Y_U')$. The background correction supplies 314 the intensity ratio of the line by itself to the background;

$$\Delta y_U = \Delta y_U' - D(\Delta y_U'). \quad (17)$$

The physical relationship between the concentration and the intensity ratio is given by the equation of the true calibration line (4), which we must now write with lower-case letters:

$$\log k = \eta \Delta y_U + \log k_U. \quad (4a)$$

Substituting (17) into (4a), we obtain the physical relationship between the concentration and the uncorrected intensity ratio $\Delta Y_U'$, i.e. the equation of the true calibration curve:

$$\log k = \eta \Delta y_U' - \eta D(\Delta y_U') + \log k_U. \quad (18)$$

Then we substitute (16) and find:

$$\log k = \frac{\eta}{f} \Delta Y_U' - \eta D\left(\frac{\Delta Y_U'}{f}\right) + \log k_U. \quad (19)$$

This is the equation of the calibration curve actually found as a result of calibration spectra; this is because we are only able to calculate the values of $\Delta Y_U'$. If we are working in a concentration range in which this curve has a pronounced curvature, we will make a background correction in order to straighten it out. Since we are not aware of the incorrect filter value, we do this with the systematically incorrect values $\Delta Y_U'$ and calculate:

$$\Delta Y_U = \Delta Y_U' - D(\Delta Y_U'). \quad (20)$$

The calculated values ΔY_U and the true values Δy_U are therefore not related by (16). This is the crucial feature.

We substitute (20) in (19) and obtain the equation of the calculated corrected calibration curve:

$$\log k = \frac{\eta}{f} \Delta Y_U + \log k_U + \eta \left[\frac{1}{f} D(\Delta Y'_U) - D\left(\frac{\Delta Y'_U}{f}\right) \right] \quad (21)$$

Were $f = 1$, i.e. if the filter value were correct, then the expression in brackets would vanish; and we would have the Equation (4a) of the true calibration line. If $f \neq 1$, the value of the expression in brackets is a function of $\Delta Y'_U$; the corrected calibration curve is also curved, and the background correction does not bring about the desired complete straightening of the calibration curve, as long as an incorrect filter value is employed in the calculation.

To see what has been achieved anyway, we wish to examine more 315 closely the form of the corrected curve (21). For large values of $\Delta Y'_U$, i.e. at relatively high concentrations, both terms in the brackets are small. At its upper end, the curve approaches the straight line

$$\log k = \frac{\eta}{f} \Delta Y_U + \log k_U.$$

The straight line passes through the fixed point of the true calibration line, but has a different slope. In our analysis with the incorrect filter value, we would find this line as the calibration line, if it were possible to measure directly the intensity of the line by itself, without the underlying background. However, we do not find it, because we are always compelled to go by way of the background correction.

For small values of $\Delta Y'_U$, i.e. for relatively low concentrations, we take the common approximation formula

$$\Delta Y' = \log x \approx 0.434(x - 1).$$

This implies $\Delta Y \approx \log \Delta Y'' + 0.362$, and by (17),

$$D(\Delta Y_U) \approx \Delta Y_U' - \log \Delta Y_U' - 0.362. \quad (22)$$

Correcting terms in the brackets in (21), and using the approximation for ΔY in the reverse direction, we finally obtain as an approximation formula for (21) in the region of low concentrations:

$$\log k \approx \eta \Delta Y_U + \log k_U - \eta \log f. \quad (23)$$

This is a calibration line with the same slope as the true calibration line, but with a fixed point shifted by $-\eta \log f$.

At both ends, the calculated calibration curve is therefore a straight line, but with the slope η/f at the upper end, and the slope η at the lower end; in between, there is a transition with continuous curvature. The calibration curve (19) for $\Delta Y_U'$, on the other hand, has the slope η/f at the upper end, but $+\infty$ at the lower end; its curvature in the transition region is therefore much greater. In any case therefore, the background correction provides a partial straightening of the calibration curve; it may be enough so that a straight-line calibration curve can be drawn in limited concentration ranges. Caution will be necessary, however, if extrapolations over larger ranges are required, as in calculating spectrochemical detection limits (see [4]).

So far we have only talked about calibration curves expressed /316 in terms of a background. What happens with calibration curves expressed in terms of a line of the base element?

For the fixed point of the true calibration line, (3) implies

$$\log k_0 = \log k_U + \eta(y_G - y_{U_2}).$$

In the equations of the calibration curves, which were calculated with the incorrect filter value, we must set

$$\Delta Y_U = \Delta Y_G + (Y_G - Y_{U_Z}) = \Delta Y_G + f(y_G - y_{U_Z}).$$

The equation for the upper asymptote of (21) then becomes

$$\log k = \frac{\eta}{f} \Delta Y_G + \log k_U + \eta(y_G - y_{U_Z}). \quad (24)$$

Hence, this line has the same fixed point k_0 as the true calibration line.

For the other asymptote (23), we find

$$\log k = \eta \Delta Y_G + \eta f(y_G - y_{U_Z}) + \log k_U - \eta \log f.$$

From it, we subtract the equation of the true calibration line expressed in terms of the base line, so that we are left with:

$$\Delta Y_G - \Delta y_G = -(f-1)(y_G - y_{U_Z}) + \log f. \quad (25)$$

This means that the lower asymptote is shifted along the horizontal axis, relative to the true calibration line, by the amount on the right side of (25).

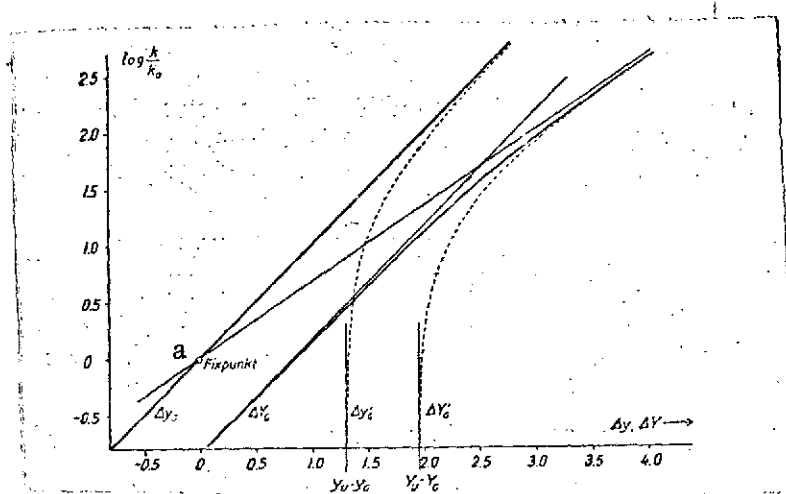
The easy way to remember this situation is: the upper asymptote passes through the same fixed point, and the lower one has the same slope as the true calibration line.

Figure 5 presents an example for calibration curves calculated with an incorrect filter value, compared with the correct curves. In this case, the error factor f is 1.5, i.e. very high, in order to make the differences stand out. This would mean, for instance, that the transmittance of a filter was taken to be 35% when it was really 50%. The slope of the true calibration line is 1.0;

$(y_G - y_{U_Z}) = -1.300$.² With these figures, the shift of the lower

² This value $(y_G - y_{U_Z}) = -1.3$ is chosen so that the different curves in the diagram will be well separated. This value would mean that the background behind the alloying-element line was 20 times as strong as the line of the base element. This could hardly occur. At any rate, such an assumption can be given an illustrative meaning: if the spectrum were taken with a step filter, and the base line in the attenuated stage compared with the alloying-element line in the unattenuated one, such a ratio would be conceivable.

asymptote relative to the true calibration line will be 0.826, by (25). This crude example shows that it is generally permissible to round off the filter value ΔY_m a bit, to make the calculations more convenient. Over reasonably small concentration ranges, the corrected calibration curves will still be sufficiently straight, and the systematic errors due to the changed slope and the lateral displacement can be compensated for in the calibration.



For the idea of the investigation described in this Appendix, I am indebted to my coworker K. Polack, and I would like to express my gratitude to him.

Fig. 5. The true calibration curves (Δy_G and $\Delta y'_G$) and the calibration curves found when an incorrect filter value is used (ΔY_G and $\Delta Y'_G$). (Slope of the true calibration line $n = 1$; error factor of the filter value $f = 1.5$; $y_G - y_{UZ} = -1.300$.)

Key: a. Fixed point

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